

## Conference Paper

# Autoclave Precipitation of Iron from Zinc Sulfate Solutions

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## Abstract

Zinc concentrates processing technology that includes high-temperature roasting – leaching of cinder – purification of leached liquor – electrowinning is the most widely used technology. Purified solution, which is fed to the electrowinning stage, has a high sensitivity to such an impurity as iron. The presence of iron in the zinc electrolyte has a negative influence both on the current efficiency and the quality of the cathode zinc. The application of autoclave equipment for iron removal from zinc sulfate solutions, obtained after the leaching stage of zinc cinder, is described in this article. All experiments were carried out with a model solution of following composition, g/L: 10-33  $H_2SO_4$ , 1.5 Cu, 5 Mn, 110 Zn, 2.5 Fe. Neutralization and purification of the solution was implemented during low-temperature pressure leaching of the zinc cinder. The optimum conditions for iron precipitation from zinc solution are following: molar flow rate  $Zn(cinder) / H_2SO_4 = 1.3$ ,  $t = 80^\circ C$ ,  $\tau = 1$  hour,  $P_{O_2} = 0.2$  MPa. It was found, that the concentration of iron can be reduced up to 1-2 mg/L, whereas 83.5% of Zn and 52.1% of Cu being recovered into the solution from zinc cinder.

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## 1. Introduction

Metallurgy of non-ferrous metals as one of the most important Ural region industries plays an important role in the structure of exports of the Russian Federation. The global output of zinc is more than 10 million tons, whereas the significant part of which is used for galvanizing [1].

The Ural deposits of polymetallic zinc ores are one of the largest deposits in the world, the proven reserves of which are about 30 million tons of metal. The main hydrometallurgical method of industrial production of zinc includes atmospheric acid leaching as the head process, the product of which is a zinc-rich solution of a complex composition. The content of certain impurities, such as iron, are undesirable due to the negative influence on target product. Therefore, the purification process is needed, which in some cases doesn't provide the appropriate rate of purification or increases the cost of the product.

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Thereby, improving the technology of zinc production at the stages of solution purification and electrowinning of zinc is relevant.

At the stage of zinc cinder acid leaching, iron is leached up to a value about 80 % [2]. The negative influence of impurities can be reflected both in the decline of the current efficiency - it leads to an increase of the electricity consumption, and in the decrease of the cathode zinc quality due to the increased content of impurities [3].

The article shows the results of autoclave purification of zinc-containing solutions from iron.

## 2. Experimental

Zinc cinder leached liquor contains  $\text{Fe}^{2+}$  ions along with  $\text{Fe}^{3+}$  ions. This fact makes the method of direct hydrolytic purification not suitable, since under these conditions  $\text{Fe}^{2+}$  ions are precipitated together with zinc ions. Consequently, preliminary increases in the redox of the system with the following neutralization are required for iron removing.

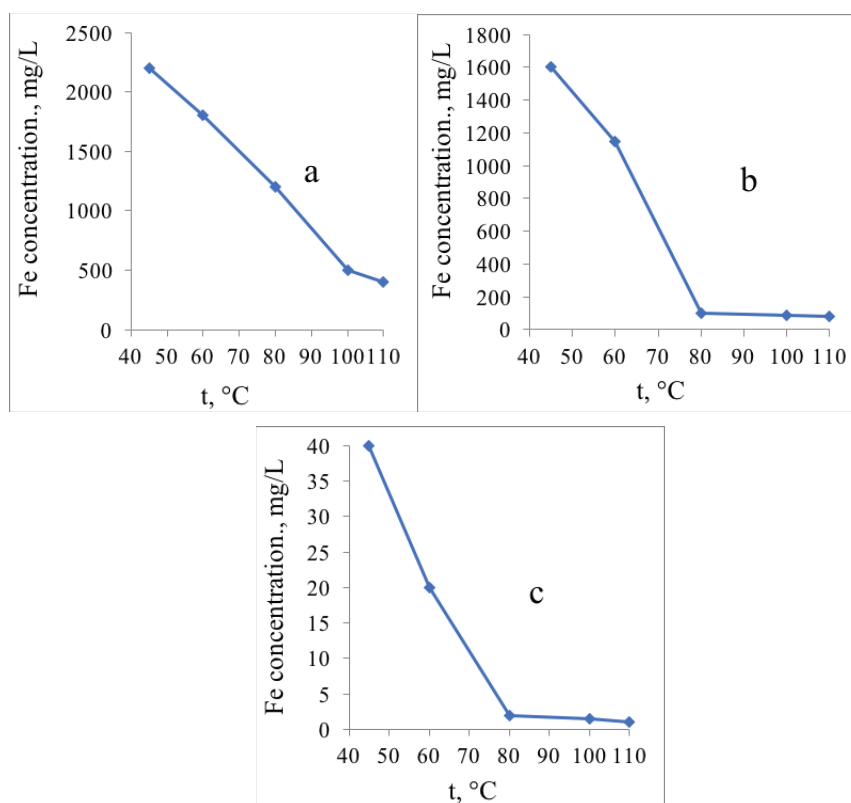
All experiments were conducted using a model solution of the following content, g/L: 10-33  $\text{H}_2\text{SO}_4$ , 1.5 Cu, 5 Mn, 110 Zn, 2.5 Fe. It was prepared from chemically pure reagents. Prepared solution fully simulated the real solutions, obtained after the zinc cinder leaching process on metallurgical plants [4].

A mixture of zinc cinder and cyclone dust in a mass ratio of 40/60 was used as a neutralizer (Table 1) and it has the following chemical composition, %: 52 Zn; 1.5 Cu; 1.1 Pb; 9.4 Fe; 0.6  $\text{S}_5$ ; 3.7  $\text{Sso}_4$ . Phase composition of mixture consists zinc in the form of  $\text{ZnO}$ ,  $\text{ZnSO}_4$ ,  $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ ,  $2\text{ZnO} \cdot \text{SiO}_2$  and  $\text{ZnS}$ , copper in the form of  $\text{CuO}$ ,  $\text{CuSO}_4$ ,  $\text{CuO} \cdot \text{Fe}_2\text{O}_3$  and  $\text{CuO} \cdot \text{SiO}_2$  and the iron presents as  $\text{Fe}_2\text{O}_3$  [5-7].

The influence of temperature, oxygen pressure and molar ratio (neutralizer/sulfuric acid) on iron precipitation and extraction of copper and zinc was investigated in the following ranges:  $t = 46-115^\circ\text{C}$ ,  $P_{\text{O}_2} = 0.0-0.4 \text{ MPa}$ ,  $\text{Zn}_{\text{cynder}} / \text{H}_2\text{SO}_4 = 0.9 - 1.4$ . Other parameters kept constant:  $\tau = 1 \text{ hour}$ ,  $[\text{H}_2\text{SO}_4]_0 = 30 - 33 \text{ g/L}$ . The aim of the experiments was to maximize the precipitation of iron.

## 3. Results and Discussion

The temperature of the process has a significant effect on the results of iron precipitation (Figure 1). Precipitation experiments at a molar ratio of  $\text{Zn}_{\text{cynder}} / \text{H}_2\text{SO}_4 = 1$  showed that with temperature increase from 45 to  $100^\circ\text{C}$ , the final concentration of iron decreases from 2,2 to 0,5 g/L. Further increasing of temperature has not such a strong effect (Figure 1a). The content of free acid at the purified solution decreased



**Figure 1:** Effect of temperature on the final concentration of iron in solution ( $\tau = 1$  hour,  $P_{O_2} = 0.2$  MPa), mole ratio of zinc cinder to sulfuric acid  $Zn_{cylinder} / H_2SO_4$ : a - 1; b - 1.15; c - 1.3.

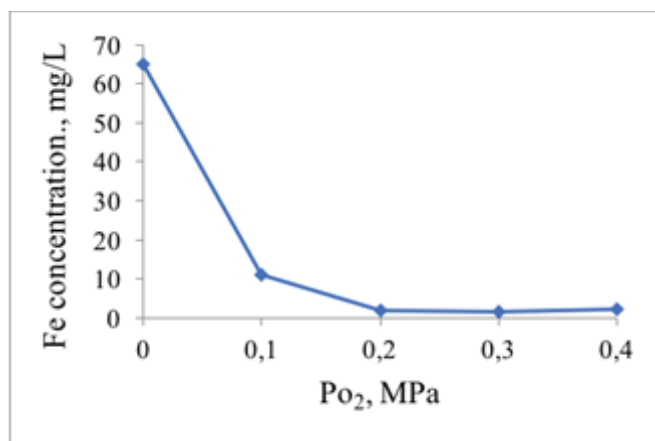
down to 0.1 - 0.3 g/L. This indicates an insufficient amount of zinc cinder for complete neutralization of sulfuric acid and explains the high content of iron in final solution.

An increase in the molar ratio  $Zn_{cylinder} / H_2SO_4$  from 1 to 1.15 had a positive effect on the precipitation of iron. With an increase in temperature from 45 to 80°C, the final concentration of iron decreases from 1600 to 100 mg/L. Further increase in temperature from 80 to 110°C has less significant impact on precipitation - the final concentration of iron declined from 100 to 80 mg/L (Figure 1a). At the end of the tests pH = 3 - 3.5.

The best precipitation results were obtained with a molar ratio of  $Zn_{cylinder} / H_2SO_4 = 1.3$ . Due to the increase in temperature from 45 to 80°C - the final concentration of iron decreased from 40 to 2 mg/L. Further increase to 110°C has less significant impact on precipitation which was 1 mg/L (Figure 1c). At the end of the experiment, the solution had a pH range 4.5-4.8. At  $t \geq 80^\circ C$ , copper hydroxide precipitation from the solution was observed.

The effect of oxygen pressure on iron precipitation is shown in Figure 2 ( $t = 80^\circ C$ ,  $\tau = 1$  hour,  $Zn_{cylinder} / H_2SO_4 = 1.3$ ).

The optimum oxygen pressure is  $P_{O_2} = 0.2$  MPa, since the final iron concentration under this conditions was 2 mg/L, and further increase the oxygen pressure up to 0.4 MPa did not effect on the precipitation of iron.



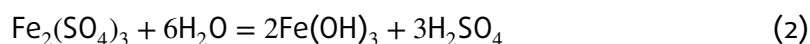
**Figure 2:** Effect of oxygen pressure on the final concentration of iron in solution ( $t = 80^{\circ}\text{C}$ ,  $\tau = 1$  hour,  $\text{Zn}_{\text{cynder}}/\text{H}_2\text{SO}_4 = 1.3$ ).

The oxidant for ions  $\text{Fe}^{2+}$  besides partial oxygen could be  $\text{Cu}^{2+}$  ions [8]:

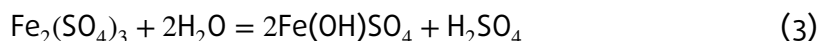


The addition of ZnO into the leached liquor, consisted of metals sulfates ( $\text{Zn}(\text{SO}_4)_2$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ), causes a sharp rise in pH as a result of neutralization reaction of the free sulfuric acid. This removes the system from hydrolysis equilibrium and accelerates the hydrolysis reaction. At the end of the experiment, the pH maximum is reached, while the dissolution of ZnO is completed and hydrolysis proceeds to form hydroxo-complexes.

In a medium with a pH of 4.8 - 5.4 and a low concentration of iron in the solution,  $\text{Fe}^{3+}$  is hydrolyzed by the reaction:



Also, basic ferric sulfates can be formed by the following reaction:

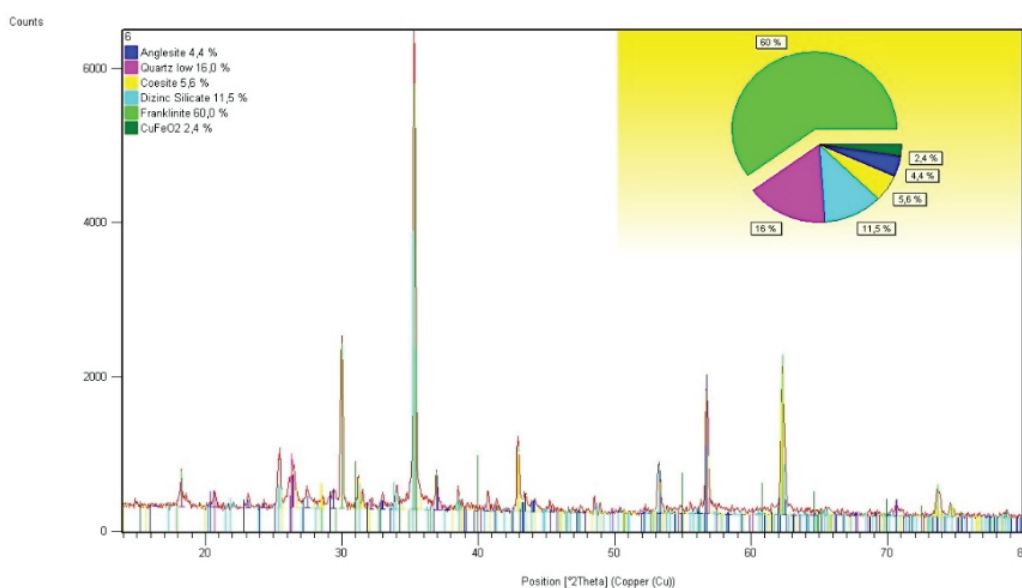


During the precipitation of iron from sulfate solutions, depending on solution composition and the process temperature, is possible to obtain the following crystalline phases:  $\text{FeOH}\text{SO}_4$ ,  $\text{FeOOH}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}(\text{OH})_3$  [9].

Thus, the optimum conditions for the precipitation of iron from the zinc solution are: molar ratio  $\text{Zn}_{\text{cynder}}/\text{H}_2\text{SO}_4 = 1.3$ ,  $t = 80^{\circ}\text{C}$ ,  $\tau = 1$  hour,  $\text{Po}_2 = 0.2$  MPa. Extraction of Zn is up to 83.5%, of Cu up to 52.1%. The final solution (pH = 4.8) has the following composition, g/L: 142 Zn, 2 Cu, 0.002 Fe.

Phase name	Chemical formula	Content, %
Franklinite	$\text{ZnFe}_2\text{O}_4$	60,0
Quartz low	$\text{SiO}_2$	16,0
Coesite	$\text{SiO}_2$	5,6
Dizinc Silicate	$\text{ZnSiO}_4$	11,5
Delafossite	$\text{CuFeO}_2$	2,2
Anglesite	$\text{PbSO}_4$	4,4

TABLE 1: Decoding of phases.



**Figure 3:** The roentgenogram of the residue ( $\text{Zn}_{\text{cynder}} / \text{H}_2\text{SO}_4 = 1.3$ ,  $t = 80^\circ\text{C}$ ,  $\tau = 1$  hour,  $\text{Po}_2 = 0.2$  MPa).

A residue after solution purification contains, %: 21 Zn, 4.2 Cu, 25 Fe, 3 Pb. The roentgenogram of the residue after leaching is presented in Figure 3. The phase interpretation and their percentage, according to X-ray phase analysis data, are presented in Table 1.

According to X-ray phase analysis data (Figure 3), the remaining zinc is in the form of  $\text{ZnFe}_2\text{O}_4$  and  $\text{ZnSiO}_4$ , as well as residues currently produced on the real plants. The residue after drying can be sent to the Waeltz process for the most complete extraction of zinc. It is logical to send the iron-free solution to the cement cleaning by zinc powder from copper and cadmium and the subsequent stage of electrolysis.

## 4. Conclusion

1. Autoclave purification allows to reduce the concentration of iron in solution from 20-50 to 1-2 mg/L for 1 hour.
2. The optimal conditions for autoclave precipitation of iron from the zinc cinder leached liquor are: molar flow  $Zn_{cylinder} / H_2SO_4 = 1.3$ ,  $t = 80^\circ C$ ,  $\tau = 1$  hour,  $Po_2 = 0.2$  MPa. The concentration of iron can be reduced down to 1-2 mg/L with simultaneous extraction of Zn (83.5 %) and Cu (52.1 %) from zinc cinder and cyclone dust mixture.
3. The autoclave purification operation of zinc sulfate solutions can be included in the current production; after the leaching, can be sent to the waxing and the solution after post-cleaning to electroextraction.

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